View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by LSBU Research Open

ANALYTICAL PYROLYSIS STUDY OF DIFFERENT LIGNIN BIOMASS

Zahra Echresh[1], Ali Abdulkhani[2], Basudeb Saha[1]
[1]Centre for Energy and Environment Research, School of Engineering, London South Bank University, 103 Borough Road, London, SE1 0AA, UK.
[2]Department of Wood and Paper Sciences and Technology, Faculty of Natural Resources, University of Tehran, Karaj, Iran.

ABSTRACT: Lignin represents about 20–30 wt% of the wood content and it is an aromatic polymer composed of phenyl propane units that are connected through ether and condensed (C-C) linkages. It is the major by-product of second-generation bioethanol production. Lignin is a main impurity in the separation of cellulose from wood for pulp and paper. Four different lignins have been selected for this study including Alcell lignin, Kraft lignin and two milled wood lignins (MWL) derived from coniferous trees (softwoods) and deciduous trees (hardwood). Pyrolysis gas chromatography (Py-GC-MS) tests were performed on each sample using CDS 5200 pyrolyser connected to a gas chromatograph with mass spectra Shimadzu GCMS. The pyrolysis products with a phenolic nature obtained by pyrolysis of all four types of lignin has reflected the nature of different lignin origins. The results have shown that more components identified by pyrolysis of MWL (hardwood and softwood) in comparison with commercial lignins (Alcell and Kraft). Components that have been observed *via* Py-GC-MS analysis indicating that degradation of all four bonds and lead to formation of three main structural units of lignin. The structural analysis of the commercial lignins revealed the partial similarity to the commercially available lignin that means raw materials contains the sufficient aromatics to be used for bio-oil production.
Keywords: Bioenergy, Biofuel, Biomass, Lignin, Pyrolysis.

1 INTRODUCTION

Fossil fuel sources are being depleted due to increased industrialisation and biomass is considered to be a sustainable source of energy for the future [1]. Conversion of biomass to biofuel has established significant consideration for the development of a renewable and environmental friendly source of energy for alternative fossil fuels since it does not contribute to greenhouse gases emission [2,3]. In addition, the fundamental issue is to develop efficient processes to convert biomass to bio-oil while producing bio-oil that meet the current fuels quality standards [4]. Biomass is an organic material that is derived from plants or animals and can be used in bio-oil production. Biomass can be divided into two main groups: virgin biomass, which includes wood, plants (lignocellulose), and waste biomass, which includes municipal solid waste (MSW) and agricultural waste [5].

Wood and other forms of biomass can be converted to biofuel using two different approaches, one involving bio-chemical methods such as fermentation and anaerobic digestion and the other one including thermo-chemical methods such as combustion, gasification, and pyrolysis [1,6,7]. Enzymatic conversion and pyrolysis are the most common methods for converting both soft and hard wood feedstock [4]. Pyrolysis is known as a process of thermal degradation of low density organic materials to vapour in the absence of oxygen [8,9]. In other words, pyrolysis is thermal decomposition of large hydrocarbon molecules to several smaller ones. The vapour is condensed to produce bio-oil and non-condensable gas phase, mainly containing CO, CO_2 and minor amounts of H_2 and CH_4. The bio-oil is stored as a source of energy and gases can be consumed to heat the pyrolysis reactor. Pyrolysis has three different variations: fast, intermediate or mild and slow pyrolysis. The mode and the conditions of pyrolysis can affect the relative proportions of the gas, liquid, and solid products [10].

The studies indicate that almost all types of biomass can be used as feedstock for pyrolysis to produce bio-oil. Cellulose, hemicellulose and lignin are the three main components of biomass. Cellulose is the most important component of biomass due to its large proportion and it contains long linear chains - (1, 4)-glycosidically linked D-glucose units [11]. However, all these three main components of biomass are determined as the elements of hydrogen, carbon and oxygen and high energy content can be relieved by pyrolysis process [12,13]. Typical lignocellulose biomass contains around 40-50 wt.% cellulose, 20–40 wt.% hemicellulose and 10–40 wt.% lignin [14] and the content of each component varies with the type of biomass [5]. Lignin occurs throughout the plant cell-wall and is mainly concentrated in the middle lamella and the primary cell-wall. Lignin is produced by plants at an annual quantity 150 billion tons and its empirical chemical formula $C_{31}H_{34}O_{11}$. It is a complex three-dimensional amorphous polymer and its degradation is different from degradation of cellulose due to its complicated structure as it is composed of many benzene rings, gives the highest char yield and its depolymerisation leads to various phenols. It is composed of three phenyl propane units: *p*-hydroxyphenyl (H), guaicyl (G) and syringyl (S)[15]. Lignin is a major impurity in the separation of cellulose from wood for pulp and paper and therefore, attracting considerable interest as a potential source of aromatic hydrocarbons for biofuels production [16]. Unlike cellulose, lignin is highly cross-linked polyphenolic polymer without any ordered repeating units. Lignin is formed by polymerisation of three monomers, named coniferyl alcohol, synapyl alcohol and *p*-coumaryl alcohol that lead, respectively, to guaiacyl (G), syringyl (S) and *p*-hydroxyphenyl propane (p-H)-type units [17]. Lignin has a high potential to replace petrochemical resources for fuel, polymers and low-molecular-weight chemical products [18].

Lignin is conventionally named based on the method of its separation from lignocellulosics material. Due to strong chemical and physical bonds between lignin and other polysaccharides of the cell wall, separation of lignin without any damage to its structure is almost impossible. Different methods of separation have been established and each method modifies to some degree the chemical structure of naturally occurring lignin. The chemical pulping processes (Kraft lignin) provide every year about 70 million tons of lignin ([19]. However, lignin is the by-product of Kraft process, steam explosion and dilute acid separation processes. The main objective of these processes is to separate the cellouse from other components of biomass.

The laboratory lignins are those that produced in the laboratory for the purpose of lignin research studies. Milled wood lignin (MWL) is isolated with dioxane from ball-milled wood after extensive extraction of extractive components. In this method of separation only minor changes occur in the structure of lignin [20].

In this study, analytical pyrolysis gas chromatography mass spectrometry (Py-GC-MS) of four different lignins has been investigated: Alcell lignin, Kraft lignin and two milled wood lignins one from coniferous trees and other from deciduous trees.

2 MATERIALS AND METHODS

2.1 Materials

Four different lignins have been selected for this study: Alcell lignin, Kraft lignin and two milled wood lignins one from coniferous trees and other from deciduous trees. Alcell lignin was provided by the Energy Research Centre of the Netherlands (ECN), which was produced *via* the organosolv pulping process. Kraft lignin was provided by Sigma Aldrich, which was solubilised by soda-sodium sulphide liquor *via* Kraft pulping process. The milled wood lignins were kindly supplied by Department of Wood and Paper Science and Technology of University of Tehran, which were extracted from wood in the laboratory and are unbroken and intact.

2.2 Preparation of Milled Wood Lignin (MWL)

The experimental part of this study for lignin preparation was performed in the laboratory of Department of Wood and Paper Sciences and Technology of University of Tehran, Karaj. According to the method provided by Abdulkhani et al (2011), first the wood pieces were crushed and then sifted with a 20 mesh size sieve. The 20 mesh sieved particles were extracted with acetone for 48 hours. After 48 hours the wood powder was treated with cold water for 10 minutes. Then the wood powder which was free of any extractives was smashed with rotary ball mill with alumina bullets in a 5 L tank for a week. In order to produce smoother particles of wood powder, the milled wood particles were grinned by a centrifuge grinder with 40 pieces of 3 mm bullet for 1 hour. The milled wood powder (MWP) were extracted with dioxane: H_2O solution (96:4, 10 ml/g) for 72 hours in a 3 stage of 24 hours each. The raw lignin was separated from the solution by a centrifuge at a rate of 8000 rpm. Subsequently, the raw lignin was separated by a freeze dryer. For the purification of the milled wood lignin (MWL), the raw lignin was settled down by diluting it in 10 ml of acetic acid (90%) and 400 ml of water. The settled lignin was dried by a freeze dryer and for a more purified lignin, the lignin was dissolved in 20 ml dichloroethane: ethanol (2:1, volume ratio) and then was settled down in diethyl ether to produce a purified lignin. Finally, the purified MWL was dried by a freeze dryer [20].

2.3 Pyrolysis gas chromatography mass spectrometry (Py-GC-MS)

Py-GC-MS tests were performed on each sample using CDS 5200 pyrolyser (CDS Analytical Pyroprobe, USA) connected to a gas chromatograph with mass spectra Shimadzu GCMS-QP2010S, Figure 1 illustrates the experimental setup. The column was mild-polarity phase, 14% cyanopropylphenyl polysiloxane; 30 m, 0.25mm inner diameter, 0.25 μm film thickness. The gas chromatograph oven was held at 40 ℃ for 2 min and then programed at 6 ℃/min 300 ℃ for a final time of 40 min and the spilt ratio was adjusted to 50:1 and gas flow rate of 0.97 ml/min.

1 mg of each lignin sample was weighed using a micro balance and then loaded in a 20 mm quartz tube between quartz wool. The lignin sample was then placed in the Pyroprobe consists of platinum coil surrounding the quart tube and pyrolised at 500 °C for 15 seconds with a heating rate of 10°C/ms. The pyrolysis products after 2 min trap *via* transfer line were directly injected into the GCMS by helium as a carrier gas. For each sample, the pyrolysis experiment was performed twice and the data are reported in the results section.

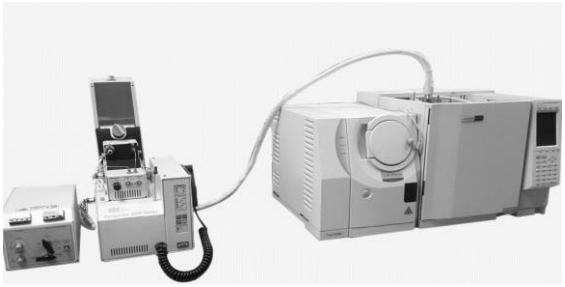

Figure 1: Gas Chromatography and Mass Spectrometry

3 RESULTS AND DISCUSSIONS

The temperature for the Py-GC-MS study was set at 500°C.The pyrolysis products yield with a phenolic nature obtained from Alcell lignin, Kraft lignin, and milled wood lignin from softwood and milled wood from hardwood have presented in Table I, II, III and IV, and the chromatogram results in the Figure 2 to 5 respectively.

Lignin is a complex polymer with a great variety of functional groups and over 10 different types of linkages [21]. The C-C bonds require higher temperature to be broken down while α-O-4 and β-O-4 linkage are easier to cleave [22].The result from this study has indicated that the breakdown of β -O-4 lead to production of three main structural monomers of lignin including; coniferyl alcohol (G) synapyl alcohol(S) and *p*-coumaryl alcohol (H). According to the analysed results, it is clear that more components identified by pyrolysis of MWL (hardwood and softwood) in comparison to commercial lignins (Alcell and Kraft) and the nature of the different lignin origins has reflected in the distribution of pyrolysis products. Alcell lignin is produced from a mixture of hardwood lignin and the two lignin monomers of hardwood: coniferyl alcohol (G) and sinapyl alcohol (S) have been presented in the pyrolysis products of this lignin. The obtained result has indicated that a higher amount of methoxyl group hardwood pyrolysis. Kraft lignin is produced from softwood, but its exact origin is not known. Thus originating the structural monomers is a bit difficult. Milled wood lignin, composed of a main monomer coniferyl alcohol (G) which has been presented in the pyrolysis products of this lignin. It indicates less amount of methoxy group compared to MWL from hardwood and MWL from softwood. 2-methoxy-4-vinylphenol, which is derived from guaiacyl group (G) with origin of coniferyl alcohol has been observed in

Table I, II and IV which indicates the hardwood origin. Phenol, 2, 6, dimethoxy-4 which is resulted from siryngyl group (S) with origin of sinapyl alcohol has been observed in Table III which illustrates the pyrolysis of softwood lignin.

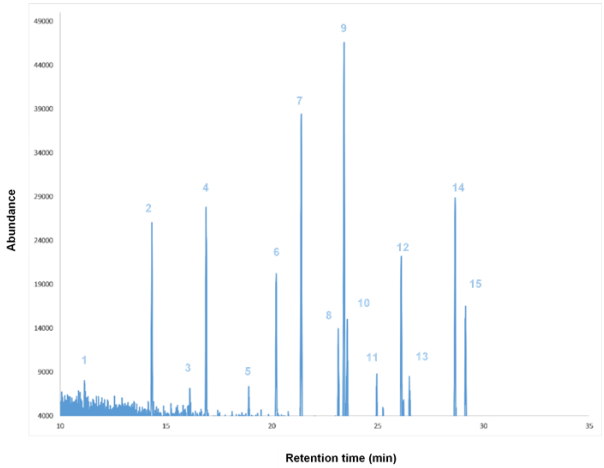

Figure 2: Chromatogram (GC-MS) resulting from pyrolysis of Alcell lignin (products are listed in Table I)

Table I: Peak identification of the pyrolysis products of Alcell lignin

Peak No	Retention Time (min)	Compounds
1	11.141	cyclohexanecarboxlic acid
2	14.325	phenol,4-methoxy
3	16.120	urea, N-(2-methoxyphenyl)
4	16.847	phenol,2-methoxy-4-methyl
5	18.884	phenol,4-ethyl-2-methoxy
6	20.218	2-methoxy-4-vinylphenol
7	21.358	3-amino-2,6-dimethoxypyridine
8	23.152	eugenol
9	23.394	phenol,4-methoxy-3 (methoxymethyl)
10	23.564	vanillin
11	24.971	phenelthylamine,3,4,5-trimethoxy
12	26.135	2,5-dimethoxy-4-ethylamphetamine
13	26.498	phenol,2,6-dimethoxy-4-(2-propenyl)
14	28.632	1,2-dimethoxy-4-(1-methoxyethyl)benzene
15	29.142	benzaldehyde,4-hydroxy-3,5-dimethoxy

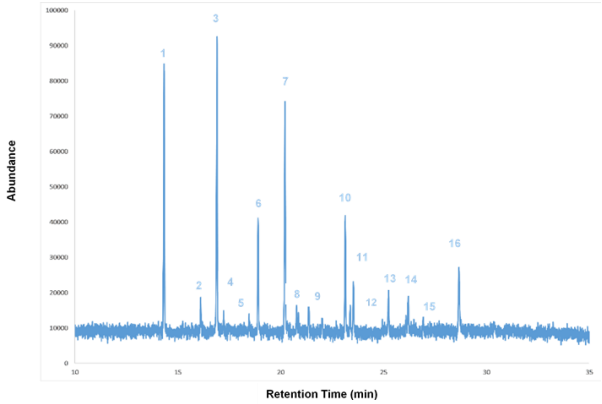

Figure 3: Chromatogram (GC-MS) resulting from pyrolysis of Kraft lignin (products are listed in Table II)

Table II: Peak identification of the pyrolysis products of Kraft lignin

Peak No	Retention Time (min)	Compounds
1	14.338	phenol
2	16.102	borazine, 1,3,5- trimethyl
3	16.932	2-methoxy-4-methyl
4	17.252	phenol-3,4, dimethyl
5	18.476	benzaldehyde
6	18.913	phenol-4-ethyl-2-methoxy
7	20.225	2-methoxy-4-vinylphenol
8	20.778	phenol,2-methoxy
9	21.390	2,4-dimethoxyphenol
10	23.139	eugenol
11	23.401	methoxymethyl
12	23.517	vanillin
13	25.237	4-hrdroxy-3-methoxyphenyl
14	26.189	1-methyl-N-vanillyl
15	26.927	vanillin acid hydrazide
16	28.653	2-hydroxy-3-ethoxy- benzyl

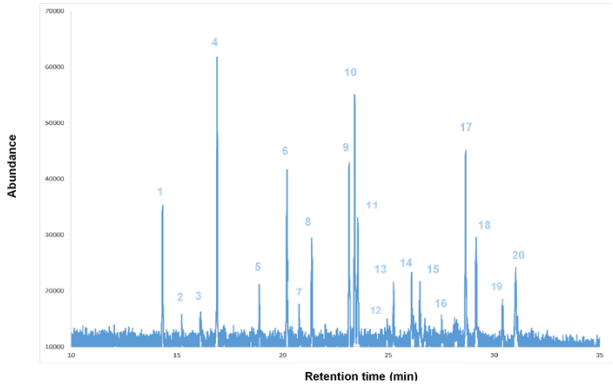

Figure 4: Chromatogram (GC-MS) resulting from pyrolysis of MWL (softwood) (products are listed in Table III)

Table III: Peak identification of the pyrolysis products of MWL (softwood)

Peak No	Retention Time (min)	Compounds
1	14.340	phenol,2 methoxy
2	15.155	2 methoxy-phenyl
3	16.123	3-hydroxy-phenethyl alcohol
4	16.888	phenol,2 methoxy-3 methyl
5	18.976	6,8 dichloro-2-methyl
6	20.244	2-methoxy-4-viniylphenol
7	20.773	phenol,2 methoxy-2-propeny
8	21.377	3-amino-2,6-dimethoxypyridine
9	23.190	phenol,2 methoxy-1-propenyl
10	23.465	Phenol, 4-methoxy
11	23.575	4-hydroxy-2-methoxy benzaldyd
12	24.953	2,4-dihydroxy-6-methoxyphenely
13	25.250	ethanone,1-4 phenyl
14	26.103	4-ethyl-2,5 dimethoxyphenylamine
15	26.511	penol,2,6 methoxy-4-phenol
16	27.556	phenol,2,6,dimethoxy-4-phenol
17	28.696	1,2-dimethoxy-4-(1-methoxyethyl) benzene
18	29.178	benzalaldehyde,4-hydroxy-3,5-dimethoxy
19	30.406	ethanone,1-(4-hydroxy-3-5-dimethoxyphenyl)
20	31.063	2-propenal,3-(hydroxyl-3methoxyphenyl)

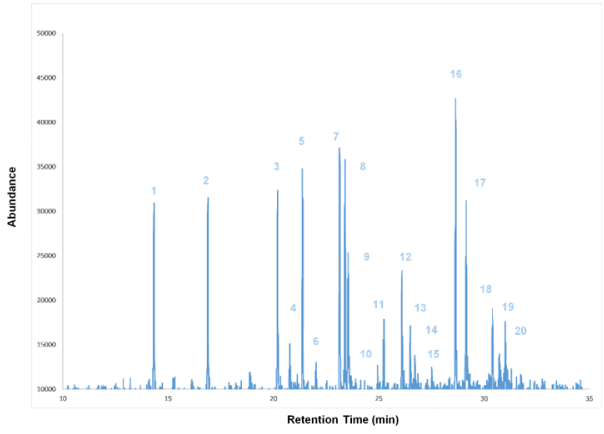

Figure 5: Chromatogram (GC-MS) resulting from pyrolysis of MWL (hardwood) (products are listed in Table IV)

Table IV: Peak identification of the pyrolysis products of MWL (hardwood)

Peak No	Retention Time (min)	Compounds
1	14.332	phenol,2-methoxy
2	16.897	phenol,2-methoxy-4-methyl
3	20.215	2-methoxy-4-vinylphenol
4	20.773	phenol,2-methoxy-2-propenyl
5	21.359	phenol,2,5-dimethoxy
6	22.028	phenol,2-methoxy-1-propenyl
7	23.227	glaucic acid
8	23.422	2,5-dimethoxybenzyl alcohol
9	23.561	vanillin
10	24.928	6-chloro-3methyl-1-indanol
11	25.262	3-hyroxy-4-methoxy phenyl
12	26.099	5-methoxy-4-methyl-2,1,3 benzothiadizole
13	26.517	1,2-dimethoxy-4-benzene
14	26.740	benzoic acid
15	27.521	2-hydroxy-4-ispropyl
16	28.664	phenol,2,6 dimethoxy-4-phenol
17	29.117	benzaldehyde
18	30.414	1,1-dimethylethyl
19	30.806	2-hydroxy-phenyl
20	31.018	4-hydroxy-3-methoxy phenyl

4 CONCLUSION

Lignin is the most abundant component in biomass after cellulose and mostly produced as residue in pulp mills industry. Lignin is a good alternative to the petroleum based polyols, which would enhance the future biofuel production. In this context, analytical pyrolysis of two commercial (from two different pulping processes) and two non-commercial lignins has been performed.

Components that have been observed *via* Py-GC-MS analysis indicating that degradation of all four lignin samples has occurred by breakage of 4-O-β bonds and lead to formation of the three main structural units of lignin. The structural analysis results of commercial lignin have revealed partial similarity to the MWL which indicates that commercial lignin contains the sufficient aromatics to be used for bio-oil production.

5 REFERENCES

[1] Jeong YW, Choi SK, Choi YS, Kim SJ. Production of biocrude-oil from swine manure by fast pyrolysis and analysis of its characteristics. Renew Energy 2015;79:14–9. doi:10.1016/j.renene.2014.08.041.

[2] Bu Q, Lei H, Wang L, Yadavalli G, Wei Y, Zhang X, et al. Biofuel production from catalytic microwave pyrolysis of Douglas fir pellets over ferrum-modified activated carbon catalyst. J Anal Appl Pyrolysis 2015;112:74–9. doi:10.1016/j.jaap.2015.02.019.

[3] Huang Y, Wei L, Crandall Z, Julson J, Gu Z.

Combining Mo-Cu/HZSM-5 with a two-stage catalytic pyrolysis system for pine sawdust thermal conversion. Fuel 2015. doi:10.1016/j.fuel.2015.02.071.
[4] Papari S, Hawboldt K. A review on the pyrolysis of woody biomass to bio-oil: Focus on kinetic models. Renew Sustain Energy Rev 2015. doi:10.1016/j.rser.2015.07.191.
[5] Stefanidis SD, Kalogiannis KG, Iliopoulou EF, Michailof CM, Pilavachi PA, Lappas AA. A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose and lignin. J Anal Appl Pyrolysis 2014. doi:10.1016/j.jaap.2013.10.013.
[6] Park HJ, Dong JI, Jeon JK, Park YK, Yoo KS, Kim SS, et al. Effects of the operating parameters on the production of bio-oil in the fast pyrolysis of Japanese larch. Chem Eng J 2008. doi:10.1016/j.cej.2007.12.031.
[7] Bridgwater A V., Peacocke GVC. Fast pyrolysis processes for biomass. Renew Sustain Energy Rev 2000. doi:10.1016/S1364-0321(99)00007-6.
[8] Yu X, Hassan M, Ocone R, Makkawi Y. A CFD study of biomass pyrolysis in a downer reactor equipped with a novel gas-solid separator-II thermochemical performance and products. Fuel Process Technol 2015. doi:10.1016/j.fuproc.2015.01.002.
[9] Chen D, Yin L, Wang H, He P. Reprint of: Pyrolysis technologies for municipal solid waste: A review. Waste Manag 2015. doi:10.1016/j.wasman.2015.01.022.
[10] Doumer ME, Arízaga GGC, Da Silva DA, Yamamoto CI, Novotny EH, Santos JM, et al. Slow pyrolysis of different Brazilian waste biomasses as sources of soil conditioners and energy, and for environmental protection. J Anal Appl Pyrolysis 2015. doi:10.1016/j.jaap.2015.03.006.
[11] Undri A, Abou-Zaid M, Briens C, Berruti F, Rosi L, Bartoli M, et al. Bio-oil from pyrolysis of wood pellets using a microwave multimode oven and different microwave absorbers. Fuel 2015. doi:10.1016/j.fuel.2015.02.081.
[12] Tsai WT, Lee MK, Chang YM. Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. J Anal Appl Pyrolysis 2006. doi:10.1016/j.jaap.2005.11.007.
[13] Kim SS, Kim J, Park YH, Park YK. Pyrolysis kinetics and decomposition characteristics of pine trees. Bioresour Technol 2010. doi:10.1016/j.biortech.2010.07.094.
[14] McKendry P. Energy production from biomass (part 1): Overview of biomass. Bioresour Technol 2002. doi:10.1016/S0960-8524(01)00118-3.
[15] Collard FX, Blin J. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. Renew Sustain Energy Rev 2014. doi:10.1016/j.rser.2014.06.013.
[16] Jiang G, Nowakowski DJ, Bridgwater A V. A systematic study of the kinetics of lignin pyrolysis. Thermochim Acta 2010. doi:10.1016/j.tca.2009.10.003.
[17] Tejado A, Kortaberria G, Peña C, Labidi J, Echeverria JM, Mondragon I. Isocyanate curing of novolac-type ligno-phenol-formaldehyde resins. Ind Crops Prod 2008. doi:10.1016/j.indcrop.2007.07.009.
[18] Brebu M, Tamminen T, Spiridon I. Thermal degradation of various lignins by TG-MS/FTIR and Py-GC-MS. J Anal Appl Pyrolysis 2013. doi:10.1016/j.jaap.2013.05.016.
[19] El Khaldi-Hansen B, Schulze M, Kamm B. Qualitative and quantitative analysis of lignins from different sources and isolation methods for an application as a biobased chemical resource and polymeric material. Anal. Tech. Methods Biomass, 2016. doi:10.1007/978-3-319-41414-0_2.
[20] Abdulkhani A, Mirshokraie A, Karimi A, Hamzeh Y. Chemical structure characterization of lignin from populus deltoides. 16th Int. Symp. Wood, Fiber Pulping Chem. - Proceedings, ISWFPC, vol. 1, 2011.
[21] Tejado A, Peña C, Labidi J, Echeverria JM, Mondragon I. Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis. Bioresour Technol 2007. doi:10.1016/j.biortech.2006.05.042.
[22] Jiang G, Nowakowski DJ, Bridgwater A V. Effect of the temperature on the composition of lignin pyrolysis products. Energy and Fuels 2010. doi:10.1021/ef100363c.

9 ACKNOWLEDGEMENTS

The authors would like to acknowledge London South Bank University and University of Tehran for supporting this research.

10 LOGO SPACE